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**(54) Process for the Recovery of
Dimethyl Terephthalate From
Polyethylene Terephthalate Polymer
Waste**

(57) A process to improve the yield of the recovery of dimethyl terephthalate (DMT) from poly (ethylene terephthalate) waste in a conventional high pressure methanolysis reaction using methanol, a suitable catalyst and high pressure to convert the polyester waste into dimethyl

terephthalate, the improvement of the process comprising the incorporation of a second catalyst capable of converting the by-product formed in the reaction into dimethyl terephthalate, thereby substantially increasing the overall yield of the reaction. The second catalyst, for example an alkaline transesterification catalyst may be added to byproduct-containing filtrate after removing solid DMT obtained with the first catalyst (e.g. zinc acetate).

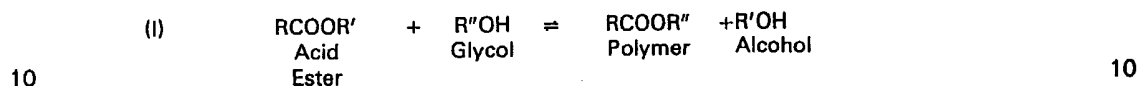
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SPECIFICATION

Process for the Recovery of Dimethyl Terephthalate from Polyethylene Terephthalate Polymer Waste

The present invention relates to a process for the recovery of dimethyl terephthalate from polyethylene terephthalate polymer waste. 5

It is known that the preparation of a polyester from a glycol and a dibasic acid is a reversible reaction which may be exemplified as follows:



wherein for poly(ethylene terephthalate),

R represents $\text{CH}_3\text{OOC-Phenyl}$, $\text{HOCH}_2\text{CH}_2\text{OOC-Phenyl}$ or $\text{H}(\text{OCH}_2\text{CH}_2\text{OOC-Phenyl-CO})_x\text{OCH}_2\text{CH}_2\text{OOC-Phenyl}$;

R' represents $-\text{CH}_3$ or $-\text{CH}_2\text{CH}_2\text{OH}$;

R'' represents HOCH_2CH_2 or $\text{H}[\text{OCH}_2\text{CH}_2\text{OOC-phenyl-CO}]_x\text{OCH}_2\text{CH}_2-$ 15

At equilibrium the amount of each of the reactants in Equation (I), above, depends upon the concentrations of the reactants present. Increased quantities of alcohol (R'OH) give increased concentrations of dibasic acid ester (e.g. dimethyl terephthalate) as the molecular weight of the polymer is reduced towards a unit degree of polymerization. The resulting glycol formed from the polymer also equilibrates to leave monomer (e.g. bis-2-hydroxy ethyl terephthalate) and lower amounts of dimer, trimer, tetramer etc. in the equilibrium mixture. The ratio of products and reactants is defined by an equilibrium constant, which varies somewhat with temperature. Catalysts effect rates of reaction without appreciable change of the equilibrium constant. 20

When polyesters are subjected to various manufacturing processes, e.g. film and fiber-making, molding of shaped objects etc., scrap is necessarily formed as a by-product. It has been the practice in the past to subject such polyester scrap to conditions whereby the polyester equilibrium reaction (Equation I) is reversed and the polyester constituents recovered so that they may be used again. For example, the usual practice has been to react the polyester scrap to equilibrium with a suitable catalyst and a lower alcohol (e.g. methanol, ethanol, or propanol, containing from 1 to 4 carbon atoms) at elevated temperature and pressure. 25 30

The dibasic acid ester (e.g. dimethyl terephthalate (DMT)) is then recovered by a rather complex and time consuming operation which requires filtration to separate the various constituents (e.g. glycol, alcohol, catalyst) from the DMT and then washing the crude alcohol-wet DMT cake with alcohol. This filtration stage removes most of the catalyst, glycol, etc. and the crude DMT cake is then distilled to remove alcohol and finally refined by vacuum distillation to give a substantially pure DMT which is useable in the manufacture of polyethylene terephthalate. The filtrate (i.e. glycol, catalyst, etc.) is also separated by distillation and reused. 35

Equilibrium studies have shown that a theoretical optimum yield of 90 percent atomic diester is predicted when one part of polyethylene terephthalate scrap is reacted with 2.5 parts by weight of a lower alcohol and a suitable catalyst. The remainder is a byproduct (U.S.P. No. 3,488,298—Eastman Kodak Company). 40

Continuing problems in such scrap recovery process, have been

- a) to isolate the by-product formed;
- b) to determine the chemical composition of by-product formed;
- c) to find a simple laboratory process to determine the percentage of this by-product formed;
- d) to find a process to convert the by-product into DMT. 45

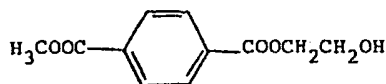
We have now developed a simple process to isolate the by-product formed, purify it, and then determine its structure, and a simple process to determine the percentage of the by-product formed. We have also developed an improved method to convert the by-product formed into DMT. 50

According to the present invention there is provided a process to improve the yield of the recovery of dimethyl terephthalate (DMT) from poly(ethylene terephthalate) waste in a conventional high pressure methanolysis reaction using methanol, a suitable catalyst and high pressure to convert the polyester waste into dimethyl terephthalate, the improvement of the process comprising the incorporation of a second catalyst capable of converting the by-product formed in the reaction into dimethyl terephthalate, thereby substantially increasing the overall yield of the reaction. 55

A preferred method of carrying out the process of the present invention is described below. The polyethylene terephthalate waste was treated with 2 to 2.5 parts by weight of methanol and about 0.4% (w/w based on the weight of waste) of zinc acetate or other suitable catalyst in an autoclave at a temperature between 180°C to 220°C and pressure of 20 kg/cm² to 25 kg/cm² for two to four hours. 60

At the end of this period the reaction mixture was cooled and was filtered under vacuum. The yield of

DMT was less than 90%. The DMT when analysed by G.L.C. was found to be more than 99% pure. The filtrate was then systematically investigated to find out the nature of the by-product formed. During the investigation it was observed that if water was added as a non-solvent to the filtrate a solid material was precipitated from the filtrate. The solid thus separated was recrystallised from benzene-hexane to give white shining crystals having a melting point of 81°C the C.H.N. analysis, IR and NMR studies and mixed melting point techniques revealed the structure of the compound to be methyl hydroxy ethyl terephthalate (MHET) having a structure



Thus, the by-product formed during the high pressure methanolysis is MHET which is structurally closely related to DMT (dimethyl terephthalate) and DGT (diglycol terephthalate), two well-known starting materials for polyester production.

The percentage of MHET formed in each high pressure methanolysis experiment was determined by the non-solvent technique explained above or by using the GLC method standardised by John Yemanis, Radmila Vilenovich and Maurice Adelman. (Gas Liquid Chromatography of silylated glycols and terephthalate esters, J. of Chromatography, 108 (1975) 79—84). It was observed that usually 11 to 22 percent MHET is formed in the high pressure methanolysis, depending upon the pressure, temperature, amount of catalyst, amount of methanol and ethylene glycol used, reaction time, and other related parameters.

It is an essential feature of our invention that this by-product MHET formed is converted almost quantitatively into DMT if the filtrate from the reaction, or even the polyester prior to filtration is refluxed or (even heated at 50°C) at atmospheric pressure for a period of 0.5 to 2 hours or more in the presence of a suitable catalyst.

The catalyst used in the above reaction is from a group of well-known transesterification catalysts such as sodium carbonate, sodium bicarbonate, calcium hydroxide or sodium hydroxide, which are all alkaline substances. The concentration of catalyst is preferably lower than one percent of the original weight of polyester waste or the concentration has to be adjusted so that pH of the reaction mixture is more than 9, preferably 10 to 12.

It is a surprising feature of our invention that MHET present in the filtrate (after removal of DMT crystals) is converted almost quantitatively into DMT if the filtrate (i.e. the filtrate containing dissolved MHET but almost free from undissolved DMT) is refluxed under pressure for about half an hour to two hours without the addition of any additional catalyst. This is mainly because during the ester interchange reaction with the alkaline catalyst the reaction often takes place at reflux temperature or even lower. However, with an acid catalyst temperatures of around 100°C are most commonly used. As the filtrate contains in addition to MHET dissolved therein an acid catalyst such as zinc acetate, and since a negligible amount of DMT is present in the filtrate a fresh equilibrium is established at 90% conversion and 90% of MHET is converted into DMT.

Our invention is clearly distinguishable from known processes, in which two catalysts zinc acetate and sodium carbonate are used in polyester waste recovery. The known process is a low pressures DMT recovery process carried out in two stages viz: glycolysis followed by methanolysis. Thus, in the prior art polyester waste was treated with ethylene glycol and zinc acetate to form oligomers of bis 2-hydroxy ethyl terephthalate. To this reaction mixture methanol and sodium carbonate were then added to converted oligomers of BHET (ESP) into DMT. However, in the process of the present invention no glycolysis is carried out and it is only a modification of the existing high pressure methanolysis process to convert the by-product formed during the reaction into DMT and thus improve the overall yield of the reaction.

Our process is of great economic value, therefore, in improving the yield of dimethyl terephthalate in the high pressure methanolysis of polyethylene terephthalate. Furthermore, in the existing high pressure process MHET formed during cracking is soluble in methanol and ethylene glycol and is processed together with the process for the recovery of methanol and ethylene glycol, and under the distillation conditions, is converted into oligomers of MHET and remains as a residue in the ethylene glycol recovery vessel. Thus, the cleaning of the ethylene glycol distillation vessel is often a problem in high pressure methanolysis process. As little or no MHET remains in the process of the invention this problem and related problems do not exist.

In order to more clearly illustrate the advantages of our invention, we offer the following specific Examples of the practice thereof. The following Examples serve to illustrate the invention but they are not intended to limit it thereto.

Example 1

100 gms of polyethylene terephthalate chips, 200 gms of methanol and 0.4 gms of zinc acetate were kept in the laboratory autoclave provided with a magnetic stirrer and were heated with stirring at 180°C and under pressure of 20—21 kg/cm² for four and a half hours. The reaction mixture was then

allowed to cool, the pressure was released, the autoclave opened and the reaction mixture was filtered under suction.

The filtrate when analysed by G.L.C. was found to contain 11.2% methyl hydroxy ethyl terephthalate. As the weight of the filtrate was approximately double the weight of the polyester, about 5 22.4% MHET was formed (based on the weight of polyester chips) as a by-product in the reaction. To 100 gms of the filtrate 1 gm of sodium carbonate was added and the filtrate was refluxed for two hours. The reaction mixture was then cooled, solid separated was filtered under suction and dried under vacuum. The weight of the dried compound was 9.6 gms, and GLC results showed this compound as DMT of 99% purity. The filtrate when analysed by GLC found to contain only 0.4 percent 10 of MHET. 10

Example 2

100 gms of polyethylene terephthalate, 250 gms of methanol and 0.4 gms of zinc acetate were kept in a laboratory autoclave provided with a magnetic stirrer and a heating arrangement. The autoclave was heated with stirring under a pressure of 20 kg/cm² for four hours. The reaction mixture 15 was then allowed to cool to room temperature, the pressure was released, the autoclave was opened and the contents were filtered under suction. 15

The filtrate when analysed by a non-solvent technique was found to contain 8.4% methyl hydroxy ethyl terephthalate. As the weight of the filtrate was approximately 2.5 times the weight of polyethylene terephthalate, about 20.6 percent MHET based on weight of polyethylene terephthalate 20 was formed as a by-product. To 100 ml of the filtrate 0.5 gms of sodium hydroxide dissolved in 5 ml of methanol was added, and the filtrate was stirred at 45°C for two hours. The solid formed was dried and weighed. The weight of the solid was 7 gms and GLC results showed this compound as 95 percent pure DMT. The filtrate when analysed by GLC was found to contain only 0.3 percent MHET. 20

Example 3

550 mgs of polyethylene terephthalate waste, 1200 gms of methanol and 2 gms of zinc acetate 25 were placed in a laboratory autoclave provided with a stirrer and a heating arrangement. The reaction mixture was heated with stirring at 180°C and a pressure of 20 kg/cm² for four hours. The reaction mixture was then cooled to 50°C and a test sample was removed from the autoclave. The filtrate when analyzed by a non-solvent technique was found to contain 11.9 percent MHET and the percentage of 30 MHET formed during the reaction based on the polyethylene terephthalate waste was 24.7 percent. 12 gms of sodium carbonate were then added to the autoclave and the reaction mixture was re-heated to 80—90°C at a pressure of 2 kg/cm² for two hours. The reaction mixture was then cooled and solids removed by centrifuging. Dried material when analysed by GLC was found to be 99 percent purity DMT. The filtrate when analysed by a non-solvent technique was found to contain only 1.3 35 percent MHET. 35

Example 4

100 gms of polyethylene terephthalate, 200 gms of methanol and 0.4 gms of zinc acetate and 1 gm of sodium carbonate were placed in an autoclave provided with a stirrer and were heated with stirring at 190°C and under pressure of 22 kgs/cm² for four hours. The reaction mixture was then 40 allowed to cool to room temperature, the pressure was released and the reaction product was recovered by centrifuging. The DMT formed an analysis was found to be of 99 percent purity. The filtrate when analysed by a non-solvent technique was found to contain 3.4 percent MHET. 40

Example 5

100 gms of polyethylene terephthalate, 200 gms of methanol and 0.4 gms of zinc acetate were 45 placed in an autoclave provided with a stirrer and were heated with stirring at 180°C and under a pressure of 20—21 kg/cm² for four and a half hours. The autoclave was then cooled to room temperature, the pressure was released and the reaction mixture was filtered under suction. 45

The filtrate when analysed by GLC was found to contain 10.1 percent MHET. A 100 gm sample of the above filtrate was then placed in an autoclave and was heated under reflux at a temperature of 50 180°C, under a pressure of 20 kgs/cm² without addition of catalyst for one hour. The autoclave was then allowed to cool and the reaction mixture filtered under vacuum. The solid material formed when dried, weighed 8.0 gms and when analysed by GLC was found to be 99 percent pure DMT. The filtrate when analyzed by a non-solvent technique was found to contain 1.2 percent MHET. 50

It is evident from the above Examples that the process of the invention is very economical to 55 operate and that it is possible to obtain an almost quantitative conversion of polyethylene terephthalate into DMT in high pressure methanolysis. 55

Claims

1. A process to improve the yield of the recovery of dimethyl terephthalate (DMT) from poly(ethylene terephthalate) waste in a conventional high pressure methanolysis reaction using 60 methanol, a suitable catalyst and high pressure to convert the polyester waste into dimethyl 60

terephthalate, the improvement of the process comprising the incorporation of a second catalyst capable of converting the by-product formed in the reaction into dimethyl terephthalate, thereby substantially increasing the overall yield of the reaction.

2. A process as claimed in Claim 1 wherein the second catalyst is a transesterification catalyst.
- 5 3. A process as claimed in Claim 2 wherein the transesterification catalyst is sodium carbonate, sodium bicarbonate, calcium hydroxide or sodium hydroxide. 5
4. A process as claimed in any one of the preceding claims wherein the concentration of the second catalyst is more than 0.5 percent of the volume of the liquor in the reaction, or more than 5% of the methylhydroxyethyl terephthalate formed during the reaction.
- 10 5. A process as claimed in Claim 4 wherein the concentration of the catalyst is adjusted to provide a reaction mixture having a pH of above 9. 10
6. A process as claimed in any one of the preceding claims wherein the second catalyst is added to the filtrate from the reaction mixture produced during the conventional high pressure methanolysis reaction.
- 15 7. A process as claimed in Claim 6 wherein the filtrate is heated to a temperature above 40°C for a period of more than half an hour. 15
8. A process as claimed in Claim 6 or Claim 7 wherein the filtrate is refluxed under pressure to convert the by-product formed during the reaction, which is in solution in the filtrate, into dimethylterephthalate.
- 20 9. A process as claimed in Claim 8, wherein the refluxing is effected at a pressure above five atmospheres. 20
10. A process as claimed in Claim 9 wherein the refluxing is effected at a pressure of from 15 to 20 atmospheres.
11. A process as claimed in any one of Claims 8 to 10 wherein the refluxing is carried out for more than half an hour. 25
12. A process as claimed in Claim 11 wherein the refluxing is carried out for from 1 to 2 hours.
13. Dimethylterephthalate whenever produced by a process as claimed in any one of the preceding claims.
14. A process to improve the yield of the recovery of dimethyl terephthalate from poly(ethylene terephthalate) waste substantially as hereinbefore described with reference to any one of the foregoing Examples. 30

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